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EFFECT OF REVERSIBILITY ON EXOEMISSION AND CORROSION OF STEEL

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Foreign Technology Division
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EFFECT OF REVERSIBILITY ON EXOEMISSION AND CORROSION OF STEEL

by

V. D. Yevdokimov and V. I. Ryaboshapchenko

FOREIGN TECHNOLOGY DIVISION

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13. ABSTRACT

The reversing (back and forth) abrasive friction of the surface of steel st.3 increased the defects of this surface and its corrosion processes to a higher degree than in case of unidirectional friction. There was also a correlation between the exoelectron emission and corrosion degree. At temps. smaller than or equal to 60 degrees the corrosion was electrochem. in nature and the oxidized film on the steel consisted of Fe_3O_4, and an intermediate product, $Fe(OH)_3$, as well as an adsorbed layer of H_2O. At temps. larger than or equal to 60 degrees the H_2O evapd. at an accelerated rate. At temps. larger than or equal to 105 degrees gaseous corrosion took place. At temps. smaller than or equal to 105 degrees as the thickness of the oxidized film decreased the exoemission increased. However at temps. larger than or equal to 105 degrees this trend decreased because of the increased work function of electrons as a consequence of the formation of a double elec. layer with the neg. side directed towards the atm.
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KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Structural Steel						
Steel Corrosion						
Metal Friction						
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Surface Phenomenon						
Crystal Defect						
Electron Emission						
Electrochemical Effect						
Thermal Effect						
Surface Film						
Iron Oxide						
Hydroxide						

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Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

EFFECT OF REVERSIBILITY ON EXOEMISSION AND CORROSION OF STEEL

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(Odessa)

It has been shown experimentally that in a reverse treatment of a surface the intensity of exoemission rises and there is an increase in the rate of steel corrosion. This pattern is also observed in heating specimens, where we see the characteristic inflections of the corrosion and exoemission curves, explained by the transition of electrochemical corrosion into gas corrosion. The intensification in the processes during reverse treatment is explained by the increased defectiveness of the surface layers.

In the above works [1-3] it was shown that the intensity of exoelectron emission from the surface of metals under friction depends on the reversibility of slip. The observed increase in exoemission during reverse friction was explained by going back to the dislocation concepts on the deformed structure of working surfaces and was studied with consideration of the prevailing chemisorption of oxygen in local concentrations of defects. Here, the surface which was more developed from the defect standpoint should after reverse friction be more intensely oxidized than a metal surface after unidirectional friction [2, 3].

Table 1. Oxidizibility of steel in air at 20°C.

(1) Время окисления, мин	(2) Толщина пленки (Å) при трении		(1) Время окисления, мин	(2) Толщина пленки (Å) при трении	
	одностороннем (3)	реверсивном (4)		одностороннем (3)	реверсивном (4)
5	2	3	30	9	11
10	5	7	40	10	13
20	7	10	50	11	15

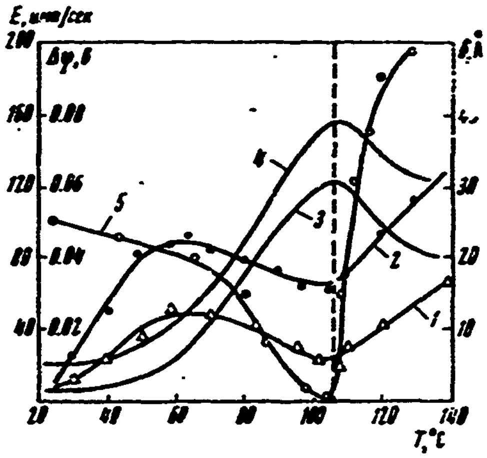
KEY: (1) Time of oxidation, min; (2) Film thickness (Å); (3) unidirectional; (4) reverse.

Presented in this report are experimental data ~~by the authors~~ on the effect of reverse abrasive friction on the initial oxidation stage of steel and on exoelectron emission. The study on exoemission with specimens in the form of rings measuring 60 × 50 × 15 mm of steel 25 was performed on the unit described in [1, 3]; the change in the thickness of the oxide film was measured by the optical polarization method[1] [4] using a goniometer. The steel surface was first cleansed with sandpaper to a class 6 finish under identical [1] unilateral and reverse friction. Here the initial surface properties of the steel remained identical, since the specimens were produced from a single rod and together underwent mechanical and thermal processing with metallographic monitoring and microhardness measuring.

Table 1 shows experimental data on the oxidation of steel 25 in air at 20°C. Reverse treatment of the steel surface increases its ability to resist corrosion. It was interesting at the same time to study the effect of the heating temperature of the specimens on exoemission and corrosion. Measurements for exoemission and thickness of the oxide film were taken under continuous heating

[1]V. Ye. Tolkachev. Study of atmospheric corrosion of several metals and alloys using the optical polarization method. Doctoral dissertation. Odessa Technological Institute, 1965.

of the circular specimens in a specially designed apparatus. The results obtained are shown in the figure, where curves 1 and 2 correspond to steel corrosion in the case of unidirectional and reverse friction, respectively, while curves 3 and 4 refer analogously to emission.



Effect of heating temperature of specimens on exoemission and corrosion.
Designation: имп/сек = imp/s.

The experimental data of curves 1-4 were processed statistically for the purpose of establishing a meaningful difference [5]. The results of calculations for averaging the curves are reduced in Table 2, where the following designations are used: S_0^2 – dispersion associated with the random factor in the observations; S_T^2 – overall sampling dispersion of all observations associated with the influence of factor T°C and with the random factor in the observations; $F = S_T^2/S_0^2$ – the Fisher distribution criterion with degrees of freedom $f_1 = k - 1$ and $f_2 = k(n - 1)$; n – a number of parallel observations (n = 5); k – levels of temperature change (11 points); P – reliability of average curve at different levels of temperature change.

The significance analysis which was conducted gives us the right to switch to a comparison of curves 1, 2 and 3, 4 (the figure) using the Student criterion to establish the effect of friction reversibility on the magnitude of change in exoelectron emission and the degree of oxidation of the steel surface. For

Table 2. Results of statistical calculation of curves (figures).

(1) № кривой	S_0^2	S_T^2	F	f_1	f_2	P, %	(1) № кривой	S_0^2	S_T^2	F	f_1	f_2	P, %
1	10.1	33.5	3.3	10	44	99	3	2229	12 700	5.7	10	44	99
2	70	170	2.4	10	44	95	4	5570	16 850	3.0	10	44	95

KEY: (1) No. of curves.

this we found the mean value of curve deviations for unidirectional and reverse friction for all levels of factor T°C from formula

$$M = \sum_{i=1}^{k} \Delta_i / k \qquad (i = 1, \ldots, k)$$

Here Δ_i is the difference between deviations in the values of exoemission and the thickness of the oxide layer for reverse and unidirectional friction, respectively, at each level; k – the number of temperature levels at which measurements were taken of exoemission and thickness of the oxide film. After the average deviation value of the curves was found the dispersion of quantity M was determined

$$m = \pm \sqrt{\sum_{i=1}^{k} (\Delta_i - M)^2 / k(k-1)}$$

Based on the Student criterion t [5] the significance of deviation M was found as $t = M/m$ for the number of degrees of freedom $f_1 = k - 1$. As a result it was learned that for exoemission $t = 4.8$, while for oxidation $t = 11$. At these values of the Student criterion the reliability of the effect of reverse friction in relation to unidirectional friction on the magnitude of change in exoemission is equal to 99.0%, to 99.9% for oxidation.

Now let us turn to the data shown in the figure. When reverse treated specimens are heated we observe an increase in the intensity of exoemission (curve 4) and corrosion (curve 2) as compared to unidirectional treatment (curves 3 and 1), which is explained by

the greater defectiveness of the surface after the reverse friction [6] with its increased lattice energy and altered work function. These curves have a characteristic inflection point at a temperature on the order of 105°C. Up to this temperature the optical method was used not only to measure the thickness of the oxide film, which has a complex structure consisting of magnetite Fe_3O_4 and the intermediate oxidation product — iron hydroxide $Fe(OH)_3$, but to determine along with it the thickness of the adsorbed water film. Starting at 60°C the water is intensely evaporated, and this process is extreme at a drying temperature on the order of 105°C, after which gas corrosion, not electrochemical, begins to develop. Corresponding to the least thickness of the film in curves 1 and 2 is the maximal excemission (curves 3, 4). It is evident that the thermostimulation of the electrons by heating of the specimens and the exothermic reaction of iron oxidation competes successfully with the protective, screening properties of the film of oxide and water, as reflected in the increased exoemission. However, after 105°C the screening effect of the oxide film becomes more noticeable with an increase in thickness, the exoelectrons begin to be absorbed by it, and the intensity of emission decreases.

In explaining the obtained data we should consider not only the change in the total thickness of the oxide and water film and its screening role, but also the physicochemical effects on the interface with the metal. Actually, the electron exchange during the process of chemical adsorption, in which the molecules of water vapor from the air or directly from the oxygen atom on the metal, has a different direction [7]. Since at low temperatures up to 105°C, when on the metal surface moisture is condensed and the adsorption of oxidizing molecules of H_2O is accompanied by a bond with the metal through the oxygen atom, there occurs a transfer of oxygen electrons to the metal. In this case the surface layer acquires a positive charge and the work function decreases. The decrease in the work function causes electron emission.

When, however, the moisture is evaporated from the surface of the metal gas corrosion begins to develop. Here we observe a transition of electrons from the metal to the oxygen with the formation of a double electric layer, whose negative surface is directed toward the atmosphere. As a result of this adsorption of oxygen the work function of the electrons from the metal increases and, consequently, the intensity of exoemission after 105°C decreases, as seen in curves 3 and 4 of the figure.

The explanation given for the inflection of exoemission curves during heating of specimens based on a change in the work function of the electrons is confirmed experimentally. Curve 5, showing the contact difference in potentials (КРП) [CDP] during the heating of steel specimens in an air medium following reverse friction, obtained by the vibrating electrode method, shows a sign change in CDP at a temperature of 100-105°C. Values $\Delta\phi$ in the figure are arranged (despite the reverse compensation sign of the potentiometer after 100°C) on one side, and reflect the nature of change in the work function. Actually, during heating (curve 5) the work function of electrons from the surface of the steel specimen at first decreases, then after the evaporation of the water and as a result of the development of gas corrosion, it rises. The zero value of $\Delta\phi$ before the sign change corresponds to the work function of electrons from a vibrating nickel reference.

Thus, the data above bring us to the conclusion that, due to the increased defectiveness of the structure [6], reverse treatment of the surface intensifies to a greater extent than unilateral treatment the corrosion processes and increases the intensity of exoemission. When steel specimens are heated this pattern is maintained, and we observe a definite correlation between exoelectron emission and corrosion.

The presence of inflections on the exoemission and oxidation curves with an increase in temperature can be explained by the

competition of physicochemical processes which occur on the metal under electrochemical and gas corrosion. Here we consider the screening properties of the film of oxide and moisture depending on their thickness.

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